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(54) ORGANIC POSITIVE TEMPERATURE COEFFICIENT THERMISTOR

(57)Abstract:
PROBLEM TO BE SOLVED: To realize characteristic of large rate of change or resistance and small hysteresis and enable easy operational temperature adjustment, by including thermosetting high molecular matrix, low molecular organic compound and conductive particles having spike-shaped protrusions.
SOLUTION: Epoxy resin, silicon resin, etc., in which oligomer with reactive epoxy group at terminal, is bridged with various kinds of hardener are used as a thermosetting high molecular matrix. Paraffin wax whose melting point is 40-100°C, vegetable wax, animal wax, fats and oils, etc., are used as low molecular organic compound. Weight of conductive particles having spike-shaped protrusions is 1.5-5 times the total weight of the thermosetting high molecular matrix and the low molecular organic compound. The conductive particles are composed of primary particles having the respective sharp protrusions. A plurality of conical spike protrusions, whose heights are 1/3-1/50 of the particle diameter, exist in one particle. Metal, especially Ni, is suitable as the material. As a result, room temperature resistance is sufficiently low, the rate of change of resistance at on-operation time and off-operation time is large, and hysteresis of temperature-resistance curve is made small.

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CLAIMS

[Claim(s)]
[Claim 1] The organic positive thermistor containing the conductive particle which has the projection of a thermosetting macromolecule matrix, a low-molecular organic compound, and the letter of a spike.
[Claim 2] The organic positive thermistor of claim 1 whose melting point of said low-molecular organic compound is 40-200 degrees C.
[Claim 3] The organic positive thermistor of claims 1 or 2 whose molecular weight of said low-molecular organic compound is 4,000 or less.
[Claim 4] One organic positive thermistor of claims 1-3 said whose low-molecular organic compounds are a petroleum system wax or a fatty acid.
[Claim 5] One organic positive thermistor of claims 1-4 said whose thermosetting macromolecule matrices are either an epoxy resin, an unsaturated polyester resin, polyimide, polyurethane, phenol resin or silicone resin.
[Claim 6] One organic positive thermistor of claims 1-5 whose weight of said low-molecular organic compound is 0.2 to 2.5 times the weight of said thermosetting macromolecule matrix.
[Claim 7] One organic positive thermistor of claims 1-6 with which the conductive particle which has the projection of said letter of a spike stands in a row in the shape of a chain.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention is used as a thermo sensor or an overcurrent protection component, and relates to the organic positive thermistor which has the PTC (positive temperature coefficient of resistivity) property that resistance increases with a temperature rise.
[0002]
[Description of the Prior Art] In this field, the organic positive thermistor which made the crystalline thermoplasticity macromolecule distribute a conductive particle is well-known, and is indicated by the U.S. Pat. No. 3243753 description, the 3351882 description, etc. A crystalline polymer expands with fusion and buildup of resistance is considered for cutting the electric conduction path of a conductive particle.
[0003] An organic positive thermistor can be used for an autogenous regulation mold heating element, an overcurrent protection component, a thermo sensor, etc. As a property required of these, it is mentioned that the room temperature resistance at the time of un-operating is low enough, that room temperature resistance and the rate of a resistance value change at the time of actuation are large enough, and that the resistance value change by repeat actuation is small.
[0004] In order to satisfy such demand characteristics, low-molecular organic compounds, such as a wax, are used and the organic positive thermistor which makes a thermoplastic macromolecule a matrix as a binder is proposed. As such an organic positive thermistor, there are a polyisobutylene / paraffin wax / carbon black system (F. Bueche, J.Appl.Phys., 44, 532, 1973), styrene-butadiene rubber / paraffin wax / carbon black system (F. Bueche, J.Polymer Sci., 11, 1319, 1973), and low density polyethylene / paraffin wax / carbon black system (KOhe et al., Jpn.J.Appl.Phys., 10, 99, 1971), for example. Moreover, a self-temperature control heating element, a ** style component, etc. using the organic positive thermistor using a low-molecular organic compound are indicated by each official report of JP,62-16523,B, JP,7-109786,B, 7-48396, JP,62-51184,A, 62-51185, 62-51186, 62-51187, JP,1-231284,A, 3-132001, 9-27383, and 9-69410. It is thought that resistance increases by fusion of a low-molecular organic compound in these cases.
[0005] When a low-molecular organic compound is used for a working substance, there is an advantage that the standup at the time of generally resistance increasing according to temperature up since degree of crystallinity is high compared with a macromolecule becomes steep. Moreover, although a hysteresis to which the direction of the temperature to which resistance usually decreases from the temperature to which resistance increases at the time of temperature up at the time of a temperature fall becomes low is shown in order that a macromolecule may tend to take a supercooling condition, this hysteresis can be suppressed by using a low-molecular organic compound. Furthermore, if the low-molecular organic compound with which the melting points differ is used, the temperature (operating temperature) to which resistance increases is easily controllable. In the case of a macromolecule, by copolymerizing with the difference in molecular weight or degree of crystallinity, and a comonomer, the melting point can change, operating temperature can be changed, but in that case, in order to be accompanied by change of a crystallized state, sufficient PTC property may not be acquired.
[0006] However, in the organic positive thermistor currently indicated by the above-mentioned reference, since carbon black and a graphite are used as a conductive particle, low initial (room temperature) resistance and big resistance rate of change are not reconciled. Although the example which resistivity (ohm-cm) increased by 108 times is shown in Jpn.J.Appl.Phys., and 10, 99 and 1971, the resistivity in a room temperature is dramatically high at 104 ohm-cm, and is not practical using especially an overcurrent protection component or a thermo

sensor. Moreover, the range of 10 or less to about 104 times has each increment in the resistance (omega) in other reference, or resistivity (ohm-cm), and it is not sufficiently low. [of room temperature resistance]
[0007] Moreover, with the melting point, when a thermoplastic macromolecule is used for a matrix, in order to soften and flow, when exposed especially to an elevated temperature, the distributed condition of a system changes, and there is a problem that a property is not stabilized.
[0008] On the other hand, the low-molecular organic compound and the organic positive thermistor using the thermosetting macromolecule as a matrix are indicated by each official report of JP,2-156502,A, 2-230684, 3-132001, and 3-205777. However, carbon black and a graphite are used as a conductive particle, these of each resistance rate of change are also as small as a single or less figure, and room temperature resistance is not reconciling not a sufficiently low thing but low initial resistance and big resistance rate of change before and behind 1 ohm-cm, either.
[0009] Moreover, not using the low-molecular organic compound, the organic positive thermistor which consists of only a thermosetting macromolecule and a conductive particle is proposed on each official report of JP,55-68075,A, 58-34901, 63-170902, JP,2-33881,A, 9-9482, and 10-4002, and U.S. Pat. No. 4966729 number descriptions. Also in these, since carbon black and a graphite are used as a conductive particle, there is no example which reconciled room temperature resistance of 0.1 or less ohm-cm and five or more-digit resistance rate of change. Moreover, generally, by the configuration of only a thermosetting macromolecule and a conductive particle, since there is no structure with the clear melting point, the standup of the resistance in a temperature-resistive characteristic becomes blunt, and the satisfactory property is not especially acquired for the application of an overcurrent protection component or a thermo sensor in many cases.
[0010] Although many carbon black and graphites had been used as a conductive particle with the conventional organic positive thermistor also including the above-mentioned thing, in order to lower initial resistance, when the fill of carbon black was made [many], sufficient resistance rate of change was not acquired, but there was a fault that it was incompatible in low initial resistance and big resistance rate of change. Moreover, although there was also an example which used general metal particles for the conductive particle, it was difficult to reconcile similarly low initial resistance and big resistance rate of change.
[0011] As an approach of solving the above-mentioned fault, the approach using the conductive particle which has the projection of the letter of a spike is indicated. The crystalline polymer, the conductive particle which specifically has the projection of polyvinylidene fluoride and the letter of a spike, and the organic positive thermistor which specifically consists of letter nickel powder of a spike are indicated by JP,5-47503,A. Moreover, the thing using nickel of the filament configuration which has the projection of the letter of a spike also on U.S. Pat. No. 5378407 descriptions, and polyolefine, an olefin system copolymer or fluoropolymers is indicated. However, in these things, although the effectiveness of reconciling low initial resistance and a big resistance change improves, since the low-molecular organic compound is not used for a working substance, the point of a hysteresis is inadequate, and it is not suitable for an application like especially a thermo sensor. Moreover, when it heats further after resistance increases at the time of actuation, there is a problem that the NTC property (negative temperature coefficient of resistivity) that resistance decreases with a temperature rise is shown. In addition, on the above-mentioned official report and the above-mentioned descriptions, using a low-molecular organic compound is not suggested at all.
[0012] Moreover, the organic positive thermistor which comes to mix thermosetting resin and the conductive particle which has the projection of the letter of a spike in JP,5-198403,A and a 5-198404 official report is indicated, and nine or more-digit resistance rate of change is acquired. However, it is difficult not to acquire sufficient resistance rate of change, if a filler fill is made [many] and room temperature resistance is lowered, but to reconcile low initial resistance and a big resistance change. Moreover, since it consists of thermosetting resin and a conductive particle, the standup of the increment in resistance is not sufficiently steep, either. In addition, it is not suggested at all that the above-mentioned official report also uses a low-molecular organic compound.
[0013]
[Problem(s) to be Solved by the Invention] Room temperature resistance is low enough, the resistance rate of change at the time of actuation and un-operating is large, the hysteresis of a temperature-system head curve is small, the NTC property after the increment in resistance is not seen, but adjustment of operating temperature is easy for the object of this invention, and it is offering an organic positive thermistor with high property stability

moreover.
[0014]
[Means for Solving the Problem] Such an object is attained by following this invention.
(1) The organic positive thermistor containing the conductive particle which has the projection of a thermosetting macromolecule matrix, a low-molecular organic compound, and the letter of a spike.
(2) The organic positive thermistor of the above (1) whose melting point of said low-molecular organic compound is 40-200 degrees C.
(3) The above (1) whose molecular weight of said low-molecular organic compound is 4,000 or less, or (2) organic positive thermistors.
(4) One organic positive thermistor of above-mentioned (1) - (3) said whose low-molecular organic compounds are a petroleum system wax or a fatty acid.
(5) One organic positive thermistor of above-mentioned (1) - (4) said whose thermosetting macromolecule matrices are either an epoxy resin, an unsaturated polyester resin, polyimide, polyurethane, phenol resin or silicone resin.
(6) said -- low-molecular -- an organic compound -- weight -- said -- thermosetting -- a macromolecule -- a matrix -- weight -- 0.2 - 2.5 -- a time -- it is -- the above -- (-- one --) - (-- five --) -- either -- an organic positive thermistor .
(7) One organic positive thermistor of above-mentioned (1) - (6) with which the conductive particle which has the projection of said letter of a spike stands in a row in the shape of a chain.
[0015]
[Function] In this invention, since the conductive particle which has the projection of the letter of a spike is used, tunnel current becomes easy to flow with the configuration, and low room temperature resistance is obtained as compared with a spherical conductive particle. Moreover, since it is large as compared with what has spherical spacing between conductive particles, a bigger resistance change is obtained at the time of actuation.
[0016] In this invention, a low-molecular organic compound is made to contain, and since the PTC (positive temperature coefficient of resistivity) property that resistance increases with a temperature rise by fusion of this low-molecular organic compound is made to discover, compared with the case where it is made to operate by fusion of a crystalline thermoplastic macromolecule, the hysteresis of a temperature-system head curve becomes small. Moreover, operating temperature can be easily adjusted by using the low-molecular organic compound with which the melting points differ compared with the case where operating temperature is adjusted using melting point change of a macromolecule etc. Moreover, the case where a thermosetting macromolecule is used as a working substance is differed from, and the standup of the resistance at the time of actuation is steep.
[0017] Furthermore, in this invention, a thermosetting macromolecule is used as a matrix. In this invention, although the big resistance change at the time of actuation has been obtained using a big cubical expansion accompanying fusion of a low-molecular organic compound, since the melt viscosity of a low-molecular organic compound is low, if it operates, the configuration of a component cannot be maintained with the configuration of only a low-molecular organic compound and a conductive particle. Therefore, in order to prevent floating by fusion of the low-molecular organic compound at the time of actuation, deformation of a component, etc., it is necessary to distribute a low-molecular organic compound and a conductive particle to a matrix macromolecule. When a thermoplastic macromolecule is used for this matrix macromolecule, since a macromolecule fuses, above the melting point, a problem is especially in high temperature oxidation stability. In this invention, since the thermosetting macromolecule is used for the macromolecule matrix and a low-molecular organic compound and a conductive particle are distributed in an insoluble and infusible three-dimension reticulated matrix, compared with the case where a thermoplastic macromolecule is used, property stability improves dramatically, low room temperature resistance and the big resistance change at the time of actuation are stabilized, and it is maintained over a long period of time.
[0018] Moreover, when a thermoplastic macromolecule matrix is used and it heats further after resistance increases, the NTC phenomenon in which resistance decreases with a temperature rise is shown. Moreover, at the time of cooling, resistance decreases from temperature higher than the melting point of a low-molecular organic compound, and the hysteresis of a temperature-system head curve is large. Especially the thing that resistance returns at temperature higher than laying temperature can become a big problem when using as a

protection component. A NTC phenomenon is a phenomenon seen also by the system which used the thermoplastic macromolecule and the conductive particle, and by continuing passing the aftercurrent which resistance increased, a conductive particle carries out a rearrangement in the matrix of a melting condition, and is considered that resistance decreases. It is considered the reason same as resistance decreasing from temperature higher than the operating temperature at the time of heating at the time of cooling. By this invention, the above-mentioned fault, i.e., the NTC phenomenon after resistance buildup, and the hysteresis of a temperature-system head curve are substantially improved by using a thermosetting insoluble and infusible macromolecule matrix.

[0019]

[Embodiment of the Invention] The organic positive thermistor of this invention contains the electric conduction child particle which has the projection of a thermosetting macromolecule matrix, a low-molecular organic compound, and the letter of a spike.

[0020] Especially as a thermosetting macromolecule matrix, although not restricted, an epoxy resin, an unsaturated polyester resin, polyimide, polyurethane, phenol resin, and silicone resin are used preferably.

[0021] An epoxy resin hardens the oligomer (from 100 molecular weight to 10,000 (about)) which has a reactant epoxy group in an end with various curing agents (bridge formation), and is classified into the glycidyl ether mold represented by bisphenol A, a glycidyl ester mold, a glycidyl amine mold, and an alicycle mold. Depending on an application, the polyfunctional epoxy resin of three or more organic functions can also be used. It is desirable to use the bisphenol A mold in these in this invention also in a glycidyl ether mold. As for the weight per epoxy equivalent of the epoxy resin to be used, 100 to about 500 are desirable. A curing agent is classified into a polyaddition mold, a catalyst mold, and a condensation mold according to a reaction mechanism. The curing agent itself adds a polyaddition mold to an epoxy group or a hydroxyl group, and it has polyamine, an acid anhydride, polyphenol, the poly mercaptan, isocyanate, etc. A catalyst mold serves as a polymerization catalyst of epoxy groups, and has tertiary amine, imidazole derivatives, etc. A condensation mold is hardened by condensation with a hydroxyl group, and has phenol resin, melamine resin, etc. It is desirable to use a polyaddition mold especially a polyamine system, and an acid anhydride as a curing agent of the bisphenol A mold epoxy resin in this invention. What is necessary is just to decide hardening conditions suitably.

[0022] Such an epoxy resin and the curing agent are marketed, for example, have Araldite by Epicoat (resin) by the oil-ized shell epoxy company, the epicure, the EPO mate (curing agent), and Ciba-Geigy etc.

[0023] An unsaturated polyester resin is what was dissolved in the vinyl monomer which commits bridge formation by the polyester (about 1000 to 5000 molecular weight) which mainly made the subject a partial saturation dibasic acid or a dibasic acid, and polyhydric alcohol, stiffens organic peroxide, such as a benzoyl peroxide, as a polymerization initiator, and is obtained. A polymerization promotor may be used together and hardened if needed. As a raw material of the unsaturated polyester used by this invention, as a partial saturation dibasic acid, a maleic anhydride and a fumaric acid are desirable, phthalic anhydride, isophthalic acid, and a terephthalic acid are desirable as a dibasic acid, and propylene glycol and ethylene glycol are desirable as polyhydric alcohol. As a vinyl monomer, styrene, diallyl phthalate, and vinyltoluene are desirable. Although what is necessary is just to decide the loadings of a vinyl monomer suitably, it is usually about 1.0-3.0 mols to one mol of fumaric-acid residue. Moreover, well-known polymerization inhibitor, such as quinones and hydroquinones, is added for the gelation prevention in a synthetic process, accommodation of a hardening property, etc. What is necessary is just to decide hardening conditions suitably.

[0024] Such an unsaturated polyester resin is marketed, for example, has the NIPPON SHOKUBAI EPO rack, the Hitachi Chemical poly set, Dainippon Ink & Chemicals Pori Wright, etc.

[0025] Although polyimide is divided roughly into a condensation mold and an addition mold by the manufacture approach, its bismaleimide mold polyimide of addition polymerization mold polyimide is desirable. Bismaleimide mold polyimide can be hardened using a reaction with homopolymerization and other unsaturated bonds, a Michael addition reaction with aromatic amine, or the Diels-Alder reaction of dienes. The bismaleimide system polyimide resin obtained by the addition reaction of bismaleimide and aromatic series diamines especially in this invention is desirable. Diamino diphenylmethane etc. is mentioned as aromatic series diamines. What is necessary is just to decide the composition / hardening condition suitably.

[0026] Such polyimide is marketed, for example, has IMIDAROI by Toshiba Chemical CORP., Ciba-Geigy

KERUIMIDO, etc.
[0027] Polyurethane is obtained by the polyaddition reaction of the poly isocyanate and polyol. As poly isocyanate, although there are an aromatic series system and an aliphatic series system, an aromatic series system is desirable and 2 and 4- or 2, 6-tolylene diisocyanate, diphenylmethane diisocyanate, naphthalene diisocyanate, etc. are used preferably. A polypropylene glycol is desirable although there are polyether polyols, such as a polypropylene glycol, polyester polyol, acrylic polyol, etc. as polyol. Although an amine system (a tertiary amine system and amine salts, such as triethylenediamine) is sufficient as a catalyst, it is desirable to use organic metal systems, such as dibutyltin dilaurate and stannous octoate. In addition, cross linking agents, such as polyhydric alcohol and a multiple-valued amine, etc. may be used together as a subsidiary material. What is necessary is just to decide composition / hardening conditions suitably.
[0028] Such polyurethane is marketed, for example, has Sumi Joule by the Sumitomo Bayer urethane company, NP series by Mitsui Toatsu Chemicals, Inc., coronate by the Japanese polyurethane company, etc.
[0029] Phenol resin makes a phenol and aldehydes, such as formaldehyde, react, is obtained, and is divided roughly into a novolak mold and a resol mold by synthetic conditions. The novolak mold generated under an acid catalyst is hardened by heating with cross linking agents, such as a hexamethylenetetramine, and the resol mold generated under a basic catalyst is hardened under heating or acid-catalyst existence by independent [its]. Whichever may be used in this invention. What is necessary is just to decide composition / hardening conditions suitably.
[0030] Such phenol resin is marketed, for example, has a stand light by Sumi Cong by Sumitomo Bakelite Co., Ltd., and Hitachi Chemical, TEKORAITO by Toshiba Chemical CORP., etc.
[0031] Silicone resin consists of a repeat of siloxane association, and has silicone rubber of the condensation in which each denaturation silicone resin, such as the silicone resin mainly obtained from hydrolysis and the polycondensation of an ORUGANO halo silane and alkyd denaturation, polyester denaturation, acrylic denaturation, epoxy denaturation, phenol denaturation, urethane denaturation, and melamine denaturation, the silicone rubber which constructed the bridge with organic peroxide etc. in linear poly dimethylsiloxane or its copolymer, and room temperature curing (RTV) are possible, and an addition mold etc.
[0032] Such silicone resin is marketed, for example, has the product made from the Shin-etsu chemistry, the Toray Industries Dow Corning make, various Toshiba Silicone silicone rubber, silicone resin, etc.
[0033] Although the resin made from heat curing to be used can be suitably chosen according to the desired engine performance and an application, it is desirable to use an epoxy resin and an unsaturated polyester resin especially. Moreover, you may be the polymerization object made to react mutually using two or more sorts.
[0034] Although it is desirable to consist of only above thermosetting resin as for a macromolecule matrix, an elastomer, thermoplastics, or its mixture may be included depending on the case.
[0035] Although there will be especially no limit if the low-molecular organic compound used for this invention is the crystalline substance of 200-800 still more preferably [molecular weight is desirable to about 4000, and] to about 1000, what is a solid-state in ordinary temperature (temperature of about 25 degrees C) is desirable.
[0036] As a low-molecular organic compound, there are waxes (specifically petroleum system waxes, such as paraffin wax and a micro crystallin wax, a vegetable system wax, an animal system wax, a natural wax like a mineral system wax, etc.), fats and oils (what is specifically called a fat or solid-state fat), etc. The component of a wax or fats and oils A hydrocarbon (-- concrete -- the straight chain hydrocarbon of a with a carbon numbers of 22 or more alkane system etc. --) -- a fatty acid (-- concrete -- the fatty acid of the straight chain hydrocarbon of a with a carbon numbers of 12 or more alkane system etc. --) -- fatty acid ester The methyl ester of the saturated fatty acid specifically obtained from with a carbon numbers of 20 or more saturated fatty acid and lower alcohol, such as methyl alcohol, etc. and (fatty-acid) amides (-- concrete -- unsaturated fatty acid amides, such as oleic amide and an erucic-acid amide, etc. --), although it is fatty amine (specifically with a carbon numbers of 16 or more aliphatic series primary amine), higher alcohol (specifically with a carbon numbers of 16 or more n-alkyl alcohol), chloroparaffin, etc. It is independent, or these very thing can be used together and can be used as a low-molecular organic compound. What is necessary is just to choose a low-molecular organic compound suitably in consideration of the polarity of a macromolecule matrix, in order to make distribution of each component good. As a low-molecular organic compound, a petroleum system wax and a fatty acid are desirable.
[0037] These low-molecular organic compounds are marketed and a commercial item can be used for them as it

is.
[0038] Since operating temperature aims at the thermistor which is 100 degrees C or less still more preferably 200 degrees C or less preferably in this invention, it is desirable that the melting point mp uses what is 40-100 degrees C still more preferably 40-200 degrees C as a low-molecular organic compound. As such a thing, it is paraffin wax (for example, 49-52 degree C of tetracosane C24H50;mp(s)). Hexa thoria KONTAN C36H74;mp73 degree C, trade name HNP-10(NIPPON SEIRO CO., LTD. make);mp75 degree C, Micro crystallin waxes, such as HNP-3(NIPPON SEIRO CO., LTD. make);mp66 degree C for example, trade name Hi-Mic-1080(NIPPON SEIRO CO., LTD. make);mp -- 83 degree C Hi-Mic-1045(NIPPON SEIRO CO., LTD. make);mp70 degree C, Hi-Mic2045(NIPPON SEIRO CO., LTD. make);mp64 degree C, Hi-Mic3090(NIPPON SEIRO CO., LTD. make);mp89 degree C, SERATTA 104(Nippon Oil purification company make);mp96 degree C, 155 micro wax (the Nippon Oil purification company make); mp70 degree C etc., a fatty acid (for example, behenic acid (Nippon Fine Chemical make);mp81 degree C and stearin acid (Nippon Fine Chemical make);mp -- 72 degree C) Palmitic acid (Nippon Fine Chemical make); mp64 degree C etc. has fatty acid ester (for example, arachin acid methyl ester (made in formation [Tokyo]);mp48 degree C etc.), a fatty-acid amide (for example, oleic amide (Nippon Fine Chemical make);mp76 degree C), etc. Moreover, there are polyethylene wax (for example, trade name Mitsui yes wax 110(Mitsui Petrochemical Industries, Ltd. make);mp100 degree C), octadecanamide (mp109 degree C), a behenic acid amide (mp111 degree C), a N-N'-ethylene bis-lauric-acid amide (mp157 degree C), N-N'- dioleoyl adipic-acid amide (mp119 degree C) and N-N'-hexa methylenebis-12-hydroxy octadecanamide (mp140 degree C), etc. Moreover, what mixed the micro crystallin wax in the combination wax which blended resin with paraffin wax, or this combination wax, and made the melting point 40-200 degrees C can be used preferably.
[0039] One sort or two sorts or more can be chosen and used for a low-molecular organic compound with operating temperature etc.
[0040] As for especially the weight of the low-molecular organic compound to be used, it is desirable that it is 0.2 to 2.5 times the sum total weight of a thermosetting macromolecule matrix (a curing agent etc. is included) of this 0.2 to 4 times. If this mixing ratio becomes small and the amount of a low-molecular organic compound decreases, resistance rate of change will become that it is sufficiently hard to be obtained. If a mixing ratio becomes large reversely and the amount of a low-molecular organic compound increases, in case a low molecular weight compound fuses, an element assembly will deform greatly, and also mixing with a conductive particle becomes difficult.
[0041] The conductive particle which has the projection of the letter of a spike used for this invention is formed from one piece and a primary particle with the projection with one sharp piece, and the projection of the letter of a spike of the shape of **** of the height of 1 / 3 - 1/50 of particle size recognizes [the particle] two or more (usually 10-500 pieces) existence at one particle. The construction material has a metal, especially desirable nickel, etc.
[0042] Although one piece and one piece may be the fine particles which exist according to an individual, as for such a conductive particle, it is desirable that about 10-1000 primary particles stand in a row in the shape of a chain, and form the aggregated particle. A primary particle may exist in a chain-like thing in part. As a former example, there is spherical nickel powder with the projection of the letter of a spike, and it is a trade name INCO. Type It is marketed as 123 nickel powder (parakeet company make), and the mean particle diameter is 3-7 micrometers. Extent and an apparent consistency are about three 1.8 - 2.7 g/cm, and specific surface area is about [0.34-0.44m] 2/g.
[0043] Moreover, as an example of the latter used preferably, there is filament-like nickel powder and it is a trade name INCO. Type It is marketed as 210, 255, 270, and 287 nickel powder (parakeet company make), among these is INCO. Type 255 and 287 are desirable. And the mean particle diameter of the primary particle is 0.1 micrometers preferably. It is or more 0.5 4.0-micrometer or less extent more preferably above. Among these, 1.0 or more micrometers [4.0] or less are the most desirable, and the mean particle diameter of a primary particle is the mean particle diameter of 0.1 micrometers to this. A less than 1.0-micrometer thing may be mixed 50 or less % of the weight above. Moreover, an apparent consistency is about three 0.3 - 1.0 g/cm, and specific surface area is about [0.4-2.5m] 2/g.
[0044] In addition, the mean diameter in this case is measured by the fish subsieve method.
[0045] Such a conductive particle is indicated by JP,5-47503,A and the U.S. Pat. No. 5378407 description.

[0046] moreover, auxiliary as a conductive particle for giving the conductivity other than the conductive particle which has the projection of the letter of a spike Carbon black, graphite, a carbon fiber, metallic-coating carbon black, Carbon system conductivity particles, such as graphite-ized carbon black and a metallic-coating carbon fiber, Metal particles, such as the shape of a globular shape and a flake, and fibrous, dissimilar metal coat metal particles (silver coat nickel etc.), tungsten carbide, titanium nitride, zirconium nitride, titanium carbide, titanium boride, and silicification -- the conductive potassium titanate whisker indicated by ceramic system conductivity particles, such as molybdenum, and JP,8-31554,A, and the 9-27383 official report may be added. As for such a conductive particle, it is desirable to carry out to 25 or less % of the weight which has the projection of the letter of a spike of a conductive particle.
[0047] As for the weight of the conductive particle to be used, it is desirable that it is 1.5 to 5 times the sum total weight (sum total weight of the organic component containing a curing agent etc.) of a thermosetting macromolecule matrix and a low-molecular organic compound. If this mixing ratio becomes small and the amount of a conductive particle decreases, it becomes impossible to make sufficiently low room temperature resistance at the time of un-operating. If the amount of a conductive particle increases reversely, big resistance rate of change will become is hard to be acquired, and the property by which uniform mixing became difficult and was stabilized will become is hard to be acquired.
[0048] Next, the manufacture approach of the organic positive thermistor of this invention is explained. First, it mixing the conductive particle which has the projection of low-molecular organic compounds, such as thermosetting resin before hardening of the specified quantity, and a curing agent, and the letter of a spike and considers as the shape of a coating dispersedly. Various agitators, a disperser, a mill, the mill for coatings, etc. are used that mixing and distribution should just be based on a known approach. Vacuum degassing is performed when air bubbles mix during mixing. For preparation of viscosity, various solvents, such as aromatic hydrocarbon, ketones, and alcohols, may be used. What slushes this into metallic foil inter-electrode, such as nickel and copper, or made it the shape of a sheet by spreading of screen-stencil etc. is hardened on the predetermined heat treatment conditions of thermosetting resin. After performing precure at low temperature comparatively at this time, there is also a method of making it an elevated temperature and performing this hardening. Moreover, a conductive paste etc. is applied to what hardened only mixture in the shape of a sheet, and it is good also as an electrode. The acquired sheet Plastic solid is pierced in a desired configuration, and let it be a thermistor component.
[0049] Moreover, various additives may be mixed in the organic thermistor of this invention as long as it does not spoil the property of this invention. For example, in order to prevent the heat deterioration of a macromolecule matrix and a low-molecular organic compound, an antioxidant can also be mixed, and phenols, organic sulfur, and FOSU fights (organic phosphorus system) are used.
[0050] Moreover, an inorganic nitride, a magnesium oxide, etc. which are indicated by the silicon nitride indicated by JP,57-12061,A, a silica, an alumina, clay (a mica, talc, etc.), the silicon indicated by JP,7-77161,B, silicon carbide, silicon nitride, beryllia, a selenium, and JP,5-217711,A may be added as a right pyroconductivity additive.
[0051] On the titanium oxide indicated by JP,5-226112,A for the improvement in endurance, ferrous oxide, a zinc oxide, a silica, magnesium oxide, an alumina, chromic oxide, a barium sulfate, a calcium carbonate, a calcium hydroxide, lead oxide, the inorganic solid-state of the high specific inductive capacity indicated by JP,6-68963,A, and a concrete target, barium titanate, strontium titanate, a niobic acid potassium, etc. may be added.
[0052] The boron carbide indicated by JP,4-74383,A for the withstand voltage improvement may be added.
[0053] The hydration titanic-acid alkali indicated by JP,5-74603,A for the improvement on the strength, the titanium oxide indicated by JP,8-17563,A, an iron oxide, a zinc oxide, a silica, etc. may be added.
[0054] the alkali halide indicated by JP,59-10553,B as a crystalline-nucleus agent, melamine resin, the benzoic acid indicated by JP,6-76511,A, a JIBEN zylidene sorbitol, a benzoic-acid metal salt, the talc indicated by JP,7-6864,A, a zeolite, a JIBEN zylidene sorbitol, the sorbitol derivative (gelling agent) indicated by JP,7-263127,A, and asphalt -- phosphoric-acid screw (4-t-buthylphenyl) sodium etc. may be added further.
[0055] As an arc accommodation control agent, the alumina indicated by JP,4-28744,B, a magnesia hydrate, the metal hydrate indicated by JP,61-250058,A, silicon carbide, etc. may be added.
[0056] As a metal damage inhibitor, IRUGA NOx MD 1024 (Ciba-Geigy make) indicated by JP,7-6864,A may

be added.
[0057] Moreover, the Lynn system compounds, such as 3 oxidization 2 antimony indicated by JP,61-239581,A, an aluminum hydroxide, a magnesium hydroxide indicated by JP,5-74603,A, an organic compound (a polymer is included) containing halogens, such as 2 and 2-screw (4-hydroxy - 3, 5-dibromo phenyl) propane and polyvinylidene fluoride (PVDF), and ammonium phosphate, etc. may be further added as a flame retarder.
[0058] Besides these, zinc sulfide, basic magnesium carbonate, an aluminum oxide, a calcium silicate, a magnesium silicate, aluminosilicate clay (a mica, talc, a kaolinite, montmorillonite, etc.), glass powder, a glass flake, a glass fiber, a calcium sulfate, etc. may be added.
[0059] As for these additives, it is desirable that it is 25 or less % of the weight of the sum total weight of a macromolecule matrix, a low-molecular organic compound, and a conductive particle.
[0060] The organic positive thermistor of this invention has the low initial resistance at the time of un-operating, it is 10-2 - 100 ohm-cm extent, and its resistance rate of change which lasts from the time of un-operating at the time of actuation is [the room temperature resistivity has the steep standup of the resistance at the time of actuation, and] as large as 6 or more figures.
[0061]
[Example] Hereafter, the example of this invention is shown with the example of a comparison, and this invention is explained concretely.
Filament-like nickel powder (the product made from INCO, trade name Type255 nickel powder) was used as a <example 1> thermosetting giant-molecule matrix as paraffin wax (the NIPPON SEIRO CO., LTD. make, trade name HNP-10, melting point of 75 degrees C), and a conductive particle as the bisphenol A mold epoxy resin (oil-ized shell epoxy company make, trade name Epicoat 801), a denaturation amine system curing agent (oil-ized shell epoxy company make, trade name EPO mate B002), and a low-molecular organic compound. The mean particle diameter of a conductive particle is 2.2-2.8 micrometers. An apparent consistency is 0.5 - 0.65 g/cm3, and specific surface area is 0.68m2/g.
[0062] 20g [of the bisphenol A mold epoxy resins], 10g [of denaturation amine system curing agents], and paraffin wax 15g (0.5 times of the sum total weight of an epoxy resin and a curing agent), nickel powder 180g (4 times of the sum total weight of an organic component), and toluene 20ml were mixed by the centrifugal type disperser for about 10 minutes. And it is 30 micrometers in thickness about the mixture of the shape of an acquired coating. After applying to one side of the electrode of nickel foil, it put with nickel foil electrode of one more sheet, and it inserted into the brass plate, and carried out to 1mm in thickness on the whole using the spacer, and heat hardening was carried out at 80 degrees C by the condition of having pressurized with the heat press machine for 3 hours. The sheet-like hardened material with which thermocompression bonding of this electrode was carried out was pierced to discoid with a diameter of 1cm, and the organic positive thermistor component was obtained. The outline sectional view of this thermistor component is shown in drawing 1 . As shown in drawing 1 , a thermistor component puts the thermistor element assembly 12 which is a sheet-like hardened material containing a low-molecular organic compound, a macromolecule matrix, and a conductive particle between the electrodes 11 formed from nickel foil.
[0063] This component was heated by 2 degrees C / min from a room temperature (25 degrees C) to 120 degrees C within the thermostat, and it cooled, and at predetermined temperature, resistance was measured by 4 terminal method and the temperature-system head curve was obtained. This result is shown in drawing 2 .
[0064] Resistance rose rapidly near 8.2x10 the melting point of 75 degrees C of -3 ohm (6.4x10-2ohm and cm) and a wax, and the resistance rate of change of initial room temperature resistance (25 degrees C) was 10 or more figures. After resistance increased, even if it continued heating to 120 more degrees C, the reduction in resistance (NTC phenomenon) was not seen. Moreover, the hysteresis was sufficiently small, without the temperature-system head curve at the time of cooling changing a lot with the thing at the time of heating.
[0065] The unsaturated polyester resin (the NIPPON SHOKUBAI make, trade name G-110AL) was used as a <example 2> thermosetting macromolecule matrix, and the filament-like nickel powder (the product made from INCO, trade name Type255 nickel powder) same as behenic acid (the Nippon Fine Chemical make, melting point of 81 degrees C) and a conductive particle as a benzoyl peroxide (the Kayaku AKZO make, trade name KADOKKUSU B-75W) and a low-molecular organic compound as an example 1 was used as organic peroxide.

[0066] 30g [of unsaturated polyester resins], 0.3g [of benzoyl peroxides], 15g [of behenic acid], and nickel

powder 180g and toluene 20ml were mixed by the centrifugal type disperser for about 10 minutes. And it is 30 micrometers in thickness about the mixture of the shape of an acquired coating. After applying to one side of the electrode of nickel foil, it put with nickel foil electrode of one more sheet, and it inserted into the brass plate, and carried out to 1mm in thickness on the whole using the spacer, and heat hardening was carried out for 30 minutes at 80 degrees C by the condition of having pressurized with the heat press machine. The sheet-like hardened material with which thermocompression bonding of this electrode was carried out was pierced to discoid with a diameter of 1cm, and the organic positive thermistor component was obtained. And the temperature-system head curve of this component was obtained like the example 1. This result is shown in drawing 3 .

[0067] Resistance rose rapidly near 5.0x10 the melting point of 81 degrees C of -3 ohm (3.9x10-2ohm and cm) and behenic acid, and the resistance rate of change of initial room temperature resistance (25 degrees C) was 8 or more figures. After resistance increased, even if it continued heating to 120 more degrees C, most reduction (NTC phenomenon) of resistance was not seen. Moreover, the hysteresis was sufficiently small at about 10 degrees C, without the temperature-system head curve at the time of cooling changing a lot with the thing at the time of heating. The hysteresis drew the tangent of the curve actuation before on the graph of a temperature-system head curve, and after actuation, made the intersection operating temperature, asked for operating temperature from the temperature-system head curve at the time of a temperature fall similarly, and considered the difference (absolute value) of both operating temperature as whenever [hysteresis].

[0068] In the <example 3> example 1 as a thermosetting macromolecule matrix Instead of the bisphenol A mold epoxy resin and a denaturation amine system curing agent Poly amino bismaleimide prepolymer (Ciba-Geigy make, trade name KERUIMIDO B601) 20g, Dimethylformamide 10g When used, and it was made to harden at 180 degrees C by 150 degrees C for 3 hours for 1 hour, and also the thermistor component was produced like the example 1 and having been evaluated similarly, the result equivalent to the thermistor component of an example 1 was obtained.

[0069] It sets in the <example 4> example 1, and is polyurethane (product made from Japanese polyurethane industry, trade name coronate) 30g as a thermosetting giant-molecule matrix instead of the bisphenol A mold epoxy resin and a denaturation amine system curing agent. When used, and it was made to harden at 100 degrees C for 1 hour, and also the thermistor component was produced like the example 1 and having been evaluated similarly, the result equivalent to the thermistor component of an example 1 was obtained.

[0070] It sets in the <example 5> example 1, and is 30g (the Sumitomo Bakelite make, trade name Sumi Cong PM) of phenol resin as a thermosetting giant-molecule matrix instead of the bisphenol A mold epoxy resin and a denaturation amine system curing agent. When used, and it was made to harden at 120 degrees C for 3 hours, and also the thermistor component was produced like the example 1 and having been evaluated similarly, the result equivalent to the thermistor component of an example 1 was obtained.

[0071] It sets in the <example 6> example 1, and is silicone rubber (Toshiba Silicone make, trade name TSE3221) 30g as a thermosetting giant-molecule matrix instead of the bisphenol A mold epoxy resin and a denaturation amine system curing agent. When used, and it was made to harden at 100 degrees C for 1 hour, and also the thermistor component was produced like the example 1 and having been evaluated similarly, the result equivalent to the thermistor component of an example 1 was obtained.

[0072] Not using <example 1 of comparison> paraffin wax, 4 times as much nickel powder as the sum total weight of an epoxy resin and a curing agent was blended, and also the thermistor component was produced like the example 1. And the temperature-system head curve of this component was obtained like the example 1. This result is shown in drawing 4 .

[0073] The room temperature resistance in early stages of this component (25 degrees C) was 8.8x10 to 3 ohm (6.9x10-2 ohm-cm), resistance increased gradually from 80-degree-C order, and a clear transition temperature was not obtained. Moreover, resistance was 13ohms at 180 degrees C, and resistance rate of change was as small as 3.2 figures.

[0074] Used <example 2 of comparison> carbon black (the Tokai Carbon make, trade name talker black #4500; mean-particle-diameter [of 60nm], and specific-surface-area 66m2/g) for the conductive particle, and 0.3 times as much carbon black as the sum total weight of an epoxy resin, a curing agent, and paraffin wax was blended, and also the thermistor component was produced like the example 1, and it evaluated similarly.

[0075] The room temperature resistance in early stages of this component (25 degrees C) was 7.2ohms (56.5

ohm-cm), resistance rose near the melting point of 75 degrees C of a wax, and resistance rate of change was 2.5 figures.

[0076] Moreover, although room temperature resistance was able to be lowered when the loadings of the above-mentioned carbon black were increased 0.5 weight twice to mixture, resistance rate of change decreased further. The effectiveness of the conductive particle which has the projection of the letter of a spike by this is clear.

[0077]

[Effect of the Invention] According to this invention, room temperature resistance is low enough, the resistance rate of change at the time of actuation and un-operating is large, the hysteresis of a temperature-system head curve is small, the NTC property after the increment in resistance is not seen, but adjustment of operating temperature is easy and, moreover, offer can be offered for an organic positive thermistor with high property stability.

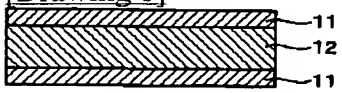
[Translation done.]

* NOTICES *

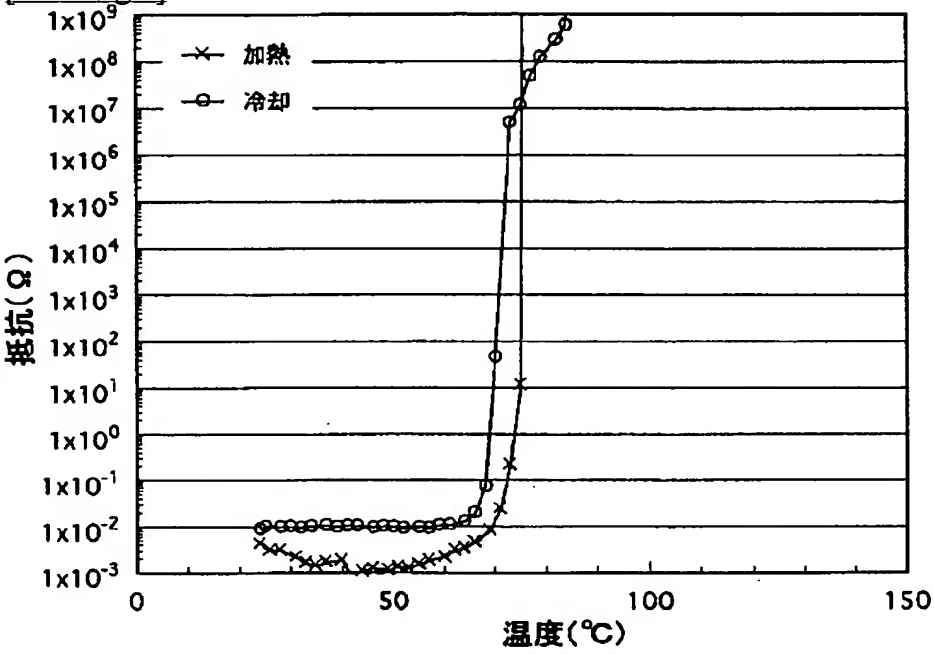
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

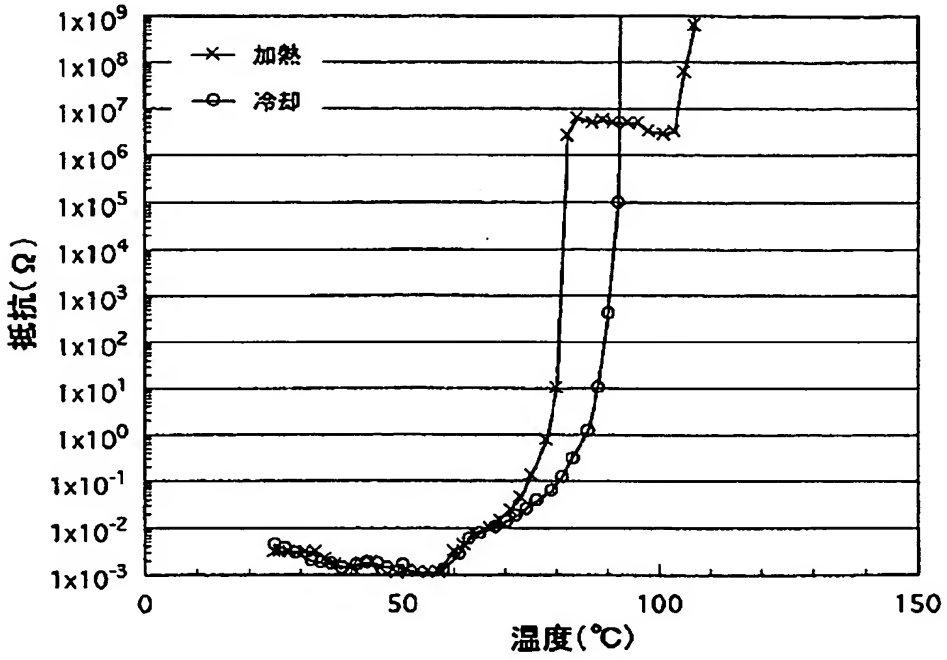
[Drawing 1]



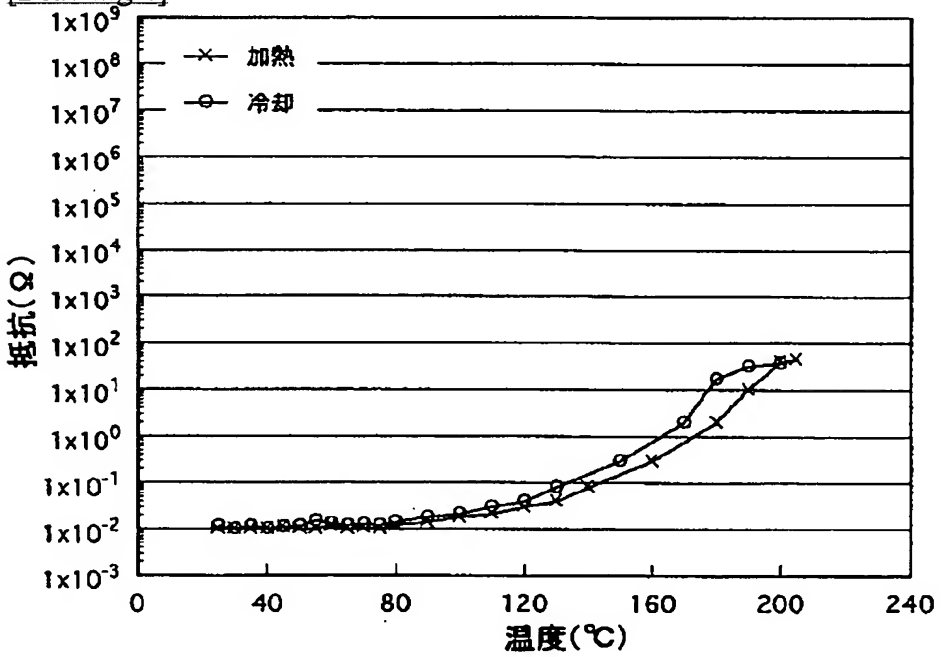
[Drawing 2]



[Drawing 3]



[Drawing 4]



[Translation done.]